

Equilibrium in the Reaction of Hydrogen with Iron Sulphide in Liquid Iron and the Thermo- dynamics of Desulphurization

By TA LI



**REPRINTED from the TRANSACTIONS of the
American Society for Metals, Cleveland, Ohio**

1936

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The free energy of FeS in liquid iron is obtained from the equilibrium measurements and the known free energy of hydrogen sulphide. Thermodynamic properties of other sulphides and oxides are obtained from data in the literature.

The data are applied to the reactions involving sulphur in the open-hearth, and to a study of several possible methods for the desulphurization of steel.

ONE of the ever present problems which the open-hearth operator must face is the control of sulphur in his product. The first essential for the production of a low-sulphur heat is the use of a low-sulphur charge and a low-sulphur fuel. When charge and fuel are kept constant, there may yet be a pronounced variation in the final sulphur content from heat to heat. The removal of sulphur from the bath by the slag, and the limitations with which this removal is beset, are qualitatively fairly well understood in most open-hearth plants. Thus, it is known that the factors which favor sulphur re-

This paper is taken from a dissertation submitted by Ta Li in partial fulfillment of the requirements for the degree of Doctor of Science at the University of Michigan. Dr. Li is now Professor of Metallurgy at the Peiyang Engineering College, Tientsin, China. Paper presented by Dr. John Chipman before the Eighteenth Annual Convention of the American Society for Metals held in Cleveland, October 19 to 23, 1936. Manuscript received June 24, 1936.

removal are a highly basic and very fluid slag, agitation at the slag-metal interface, a high temperature, and, in the basic electric furnace, complete freedom from active oxides. The influence of other variables is less clearly understood, and in spite of the progress that has been made in the chemistry of the open-hearth process, there is no broad general method for estimating quantitatively the desulphurizing power of a slag.

It seems reasonable to anticipate that the application of thermodynamic methods will contribute to our understanding of the behavior of sulphur in the refining of steel. At the same time, it may not be out of order to express the hope that it will lead ultimately to more effective control of sulphur in open-hearth operation.

The thermodynamic data necessary for attacking the problem of the behavior of sulphur can, for convenience, be subdivided in accordance with the three phases in which sulphur occurs. First, there is the gas phase, in which sulphur may occur as H_2S , S_2 , or SO_2 , the other possible compounds being of minor importance. Second, is the slag phase in which the major portion of the sulphur exists as metallic sulphides. Finally, there is the liquid metal in which the sulphur is dissolved, presumably as iron sulphide. The published information on the iron-sulphur system has recently been reviewed by Benedicks and Lofquist (1).¹ They show that iron sulphide is miscible with liquid iron in all proportions. The system is, therefore, very different from the iron-oxygen system, and methods which are applicable to the one may be entirely inapplicable to the other. Nevertheless, it will be shown in a later section of this paper that like oxygen the sulphur in liquid iron exists as a compound whose molecule contains a single atom of sulphur, and whose formula is, therefore, most simply written FeS . The key to the thermodynamic study will be found in this compound, FeS , as it exists in liquid steel. Its properties in this condition cannot be obtained with accuracy by extrapolation of data from lower temperatures, partly because of conflicting data, but more especially because of a complete lack of knowledge as to the ideality or nonideality of the solution. Its most important thermodynamic property, the free energy, can be obtained from an experimental study of its equilibrium with other substances for which this quantity has been accurately established. The properties of hydrogen sulphide are known with a high degree of accuracy, and since it is easily handled, and may be accurately deter-

¹The figures appearing in parentheses refer to the bibliography appended to this paper.

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PRICE 45 CENTS

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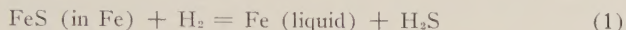
removal are a highly basic and very fluid slag, agitation at the slag-metal interface, a high temperature, and, in the basic electric furnace, complete freedom from active oxides. The influence of other variables is less clearly understood, and in spite of the progress that has been made in the chemistry of the open-hearth process, there is no broad general method for estimating quantitatively the desulphurizing power of a slag.

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mined, it appeared to be the ideal substance for the purpose. The reaction by which it is formed from iron sulphide in liquid iron is,



The main object of the experiments described in this paper was to determine the condition of equilibrium in this reaction, and thereby to establish the free energy of FeS in liquid iron at steel-making temperatures.

EXPERIMENTAL METHOD

In brief, the principle of the method employed was as follows: An alloy of iron and sulphur is melted in the high frequency induction furnace in a gaseous mixture of hydrogen and hydrogen sulphide. When the sulphur content of the alloy attains a constant value, and when the composition of the gas flowing from the furnace is the same as that flowing into it, equilibrium has been established, and the equilibrium constant can be obtained from the analysis of the gas and of the metal.

Furnace—The induction furnace is shown in Fig. 1. The crucible N holds 50 to 80 grams of metal. It is supported by the silica tube M, and the pyrex tube L. The silica tube A, about two inches outside diameter, is fitted with water-cooled, brass ends. The lower crucible K is used to catch any metal that is dropped by failure of the melting crucible. The gas stream enters at the top through E and passes out through J. In order to avoid any errors occasioned by thermal diffusion such as those observed in analogous experiments with hydrogen and steam (2), the entering gas was preheated by the molybdenum filaments F. These filaments were electrically heated to approximately the temperature of the metal. They were not corroded by the gaseous mixture, although they became rather brittle after repeated use. It was shown by blank runs, in

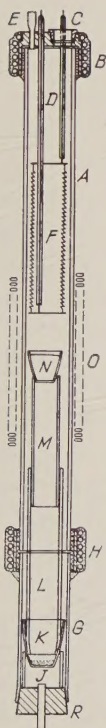


Fig. 1—Induction Furnace. N—Melting Crucible. O—Induction Coil. A—Silica Tube. E—Inlet. J—Outlet. F—Preheating Filament.

which no iron was charged, that the heated filaments did not affect the composition of the gas.

Temperature Measurements—Temperatures were measured by sighting an optical pyrometer of the disappearing filament type through the pyrex window C. This pyrometer had been previously calibrated, and was occasionally rechecked against the melting point of electrolytic iron in the crucible N. The melting point of this iron was taken as 1530 degrees Cent. (2785 degrees Fahr.).

Gas Mixture—Preliminary calculation showed that a gas mixture containing about 1000 times as much hydrogen as hydrogen sulphide should be in equilibrium with metal containing a few tenths of a per cent sulphur. Gas mixtures were prepared under pressure in a steel cylinder which previously had been used for hydrogen. A manifold system fitted with valves and gages was used to connect this cylinder to a small cylinder of hydrogen sulphide, a full cylinder of hydrogen, and a vacuum pump. The cylinder was first evacuated, then hydrogen sulphide was admitted up to any desired pressure, say 0.3 atmosphere as measured on a mercury manometer. Hydrogen was then added to bring the total pressure up to 60 or 70 atmospheres. After standing for several days, during which the cylinder was occasionally inverted, the mixture became very uniform. When the cylinder was first used for this purpose, it walls absorbed a large amount of hydrogen sulphide, resulting in a much lower concentration than was desired. However, after several fillings, a state of saturation was attained, and no further trouble was encountered. The analysis of the mixture was always checked before and after using.

Iron-Sulphur Alloy—After a few preliminary runs in which electrolytic iron was used, it was found convenient to use an alloy of iron and sulphur as the starting material. This alloy was prepared in small batches by melting electrolytic iron in a magnesia crucible in vacuum and adding iron sulphide to the melt. Commercial iron sulphide was used in preparing low-sulphur alloys, but for the higher sulphur contents, a synthetic material, formed by heating flowers of sulphur with electrolytic iron filings, was employed. In several runs the residues of ingots from previous experiments, after sampling for analysis, were employed. The use of iron-sulphur alloys, rather than pure iron, as the starting material, decreased the time required for reaching equilibrium, and also permitted the equilibrium state to be approached from both sides.

Methods of Analysis—The evolution method, with some modifications to promote accuracy, was adopted for the analysis of the alloys and the gaseous mixtures. For sulphur in iron, the sample was first dissolved in dilute hydrochloric acid, and the evolved gas was passed through an ammoniacal solution of cadmium chloride contained in a ten-bulb absorber. The solution flask and absorber were swept out with tank hydrogen before and after solution of the sample. The solution containing the precipitated cadmium sulphide was acidified and allowed to react with an excess of standard potassium iodate solution. The excess iodine was then titrated with standard sodium thiosulphate.

For the gaseous mixture, the gas was drawn through the same absorber, and its content of hydrogen sulphide was determined in the same way. The hydrogen left after absorption was collected over dilute acid, and its volume, after correcting for aqueous tension, was reduced to standard conditions. The molal ratio of H_2S to H_2 was then readily computed. The use of the same method of analysis for the gas and the alloy should virtually nullify any systematic errors in the analytical work.

Sampling—The amount of sample used in the evolution method, should not produce, in the absorbing solution, an amount of cadmium sulphide (CdS) that will require more than 20 cc. of iodate solution. Hence for a sample containing about 1 per cent sulphur, a 0.5 gram sample is a suitable amount to be used in each analysis. For 0.5 per cent sulphur, not more than 2 grams should be used. For sulphur below 0.1 per cent, 5 grams may be used. Therefore, it is evident that special precautions must be taken in order to obtain a representative sample, especially when a very small amount is to be used.

Iron with FeS inclusions is far more brittle than the iron itself. When such a sample is made into filings by drilling, turning, or sawing, the fine particles produced contain more FeS than the coarser ones. For example, the melt from Run 51 was sawed into several pieces by running the saw vertically through the center of the melt. Five analyses were made from these saw filings, the results of which were: 0.667, 0.669, 0.668, 0.640, and 0.667 per cent sulphur. The value adopted was 0.668 per cent sulphur. The remainder of the saw filings were sifted on a 60-mesh sieve. The part retained on the sieve gave an analysis of 0.631 per cent sulphur, while the part which passed through gave 0.715 per cent sulphur.

FeS inclusions may not be distributed uniformly throughout the iron. A number of samples have been polished and examined under the microscope. For a sound melt, or a sample with a single hollow space (pipe) in the middle, the grain size of the iron was uniform, and the FeS which filled out the grain boundaries was distributed uniformly throughout the sample, as shown in Fig. 2. But for a highly porous melt, as those usually obtained from the runs with quartz crucibles, the distribution of FeS was not uniform. The FeS was usually concentrated at the end of each blow hole. Since the blow holes pointed toward the center of the melt, there usually resulted a higher per cent of sulphur in the center than at the edges. In a melt containing sulphur below 0.1 per cent, the FeS existed as elongated globulous forms, and was not distributed uniformly (Fig. 3), even when the melt itself was not very hollow or porous. The following three analyses illustrate very well this segregation of FeS when the sample is porous or when the per cent of sulphur is low:

Run 50—Melt, hollow and porous.

	Per Cent Sulphur
Portion sawed off horizontally at the center	0.618
Portion sawed off vertically at the edge	0.473
Mean values from several analyses of lathe turnings	0.520

Run 55—Melt, hollow and porous. Half of the melt was turned horizontally into three portions.

	Grams	Per Cent Sulphur
Filings from the top	5.0	0.096
Filings from the middle	5.0	0.101
Filings from the bottom	4.0	0.094
Weighted average		0.097

Run 57—Melt, hollow. Half of the melt was lathed vertically into three portions.

	Grams	Per Cent Sulphur
Filings from the outer portion	10.762	0.0934
Filings from the intermediate portion	9.362	0.1033
Filings from the center portion	9.362	0.1033
Weighted average		0.101

Taking these precautions into consideration, most of the melts were sampled by turning them out vertically on a lathe, with a sharp tool, into uniform filings. These were received on a piece of paper spread under the tool, until half of the melt had been consumed. The

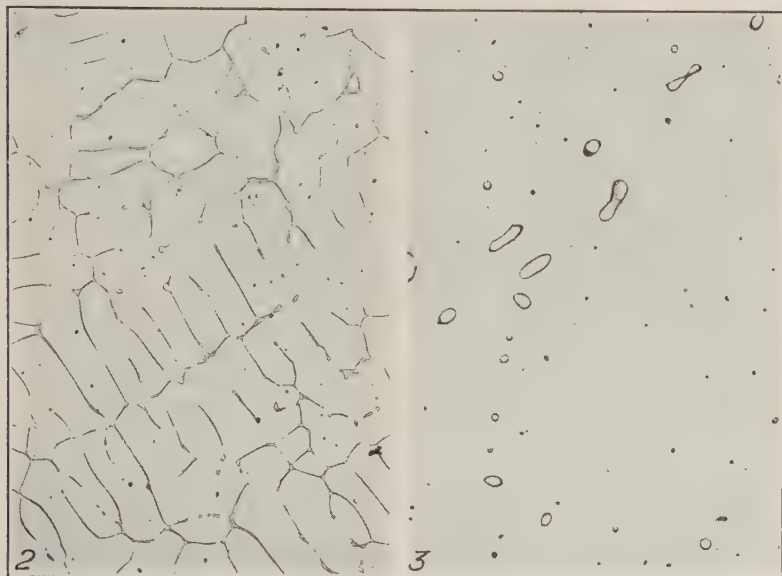


Fig. 2—Iron Sulphide Inclusions in Heat 22. 0.976% S. $\times 100$.
Fig. 3—Iron Sulphide Inclusions in Heat 58. 0.0925% S. $\times 500$.

filings were then mixed thoroughly and the necessary amount weighed out for analysis. If two or three analyses did not give check results, then the determinations were repeated. In many melts from the runs using quartz crucibles, all the filings had to be analyzed, and the weighted average was taken to represent the per cent sulphur in the melt. For a sound sample or a sample with a single pipe, it was usually sawed vertically into halves, and the filings recovered. All the filings which amounted to only 1 to 2 grams were analyzed.

EQUILIBRIUM DETERMINATIONS

The method of carrying out a determination may be briefly described as follows: 50 to 70 grams of the sample was weighed out into the crucible and placed in the furnace. The gas mixture was passed through the furnace for 15 minutes or more, and the power was turned on. After the sample had melted the power input was reduced so that a slow solidification occurred during which the temperature was observed. In the case of the electrolytic iron melts this observation constituted a valuable check on the calibration of

Table I
Preliminary Runs With MgO Crucibles

Run	Duration of Run in Hrs.	Temper- ature in °C.	Rate of Gas in CC./Min.	$\frac{\text{H}_2\text{S}}{\text{H}_2} \times 10^3$		% S in Iron	Ratio $\frac{\text{H}_2\text{S}}{\text{H}_2} \times 10^3$	
				Entering			$\text{H}_2 \times \% \text{S}$	
9	0.5	1600	400	4.38		0.062	72.9	
8	1.0	1600	430	4.66		0.184	25.3	
3	1.3	1600	500	1.34		0.051	26.3	
4	1.4	1605	500	5.02		0.204	24.6	
12	3.0	1600	450	3.61		0.284	12.7	
13*	2.0	1600	400	3.61		0.175	20.6	
6	1.0	1558	500	4.97		0.124	40.1	
10	2.0	1558	500	4.44		0.315	14.1	
11	3.9	1558	500	2.84		0.233	12.2	
14	5.0	1558	400	4.24		0.447	9.5	
5	1.0	1667	500	4.71		0.130	36.2	
7	1.3	1759	400	4.97		0.145	34.2	

*Preheating filament was not heated up.

the pyrometer. During the melting period, the inlet gas was analyzed. The melt was then brought to the desired temperature and the gas stream to the desired rate of flow. These and the filament temperature were adjusted every five or ten minutes during the run. The outlet gas from the furnace was analyzed every 20 to 30 minutes.

When the time of the run was finished, the power was stopped suddenly and the solidification occurred within a few seconds. The ingot was cooled in the furnace to room temperature, then removed and sampled for analysis.

Preliminary Runs—Time to Reach Equilibrium

Table I gives the results of a set of preliminary runs using magnesia crucibles, starting with pure iron, at a rate of gas kept at about 500 cubic centimeters per minute, and the composition of gas from 3 to 5 volumes of H_2S in 1000 volumes of H_2 . The varying factors that can be studied are the time of run, the temperature of run and the preheating of the gas.

Fig. 4 shows the increase of sulphur in iron with the time of run. Only those runs with higher gas ratios are plotted. Runs 3 and 11, in which the gas has a low ratio, and Run 13, in which the gas is not preheated, are not shown. Since the gas composition and the gas rate were not kept strictly constant, and since it will subsequently be shown that the magnesia crucible itself will absorb some H_2S from the gas, this plot should not be taken to represent the phenomena with any exactness. But qualitatively, this plot, together with Table

I, and observations made during these experiments, does indicate the following facts:

1. There is no evidence of any kind as to the deposition of liquid or solid sulphur in the cold part of the furnace. This confirms preliminary calculation that the gas mixture passing through the furnace should not be decomposed.

2. There is no apparent reaction between the crucible and the FeS or Fe in the melt, for the crucibles after the run al-

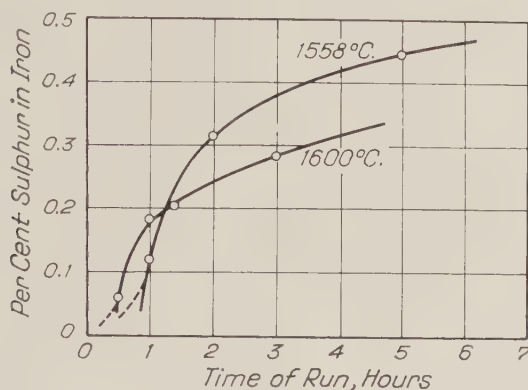


Fig. 4—Increase in Sulphur in Iron with Time of Run.

ways give a clean and white inside surface where it has been in contact with the liquid melt during the run (see Fig. 5).

3. The preheating of the gas mixture has a decided effect on the amount of sulphur absorbed by the iron in such a manner that the lower the temperature to which the gas is preheated, the lower the amount of sulphur which will be absorbed by the iron.

4. The limiting amount of sulphur in iron absorbed from a given gas mixture increases as the temperature decreases.

5. The final and the most important fact is, that, from the shape of the curves plotted, the time for reaching the final equilibrium state would be exceedingly long. For this reason, it was not attempted to reach the equilibrium beginning with pure iron.

Runs with Magnesia Crucibles—From the results of the preliminary runs, it is seen that when starting with pure iron, the time for reaching the final equilibrium is exceedingly long. The equi-

librium can be reached from the low sulphur side more quickly, and just as surely, by starting with an iron-sulphur alloy containing somewhat less than the equilibrium amount of sulphur. It can also be reached from the high sulphur side by beginning with a slightly higher sulphur content.

Table II gives the results of a series of runs using magnesia crucibles, with an initial amount of sulphur in the melt, and a higher gas rate. The first four runs, namely, 15, 16, 17 and 18, give the

limits within which the equilibrium constant
$$K' = \frac{(H_2S)}{(H_2) \times (\% S)}$$

should lie. All the subsequent runs, especially those at 1558 degrees Cent., give fairly close values of K' , indicating that equilibrium is reached at these values. The final results would have been obtained at this stage, were it not for the fact the analysis of the outlet gas near the end of each run always gave a constant value which is lower than that of the inlet gas.

Attempts were made to find the causes of this decrease of H_2S in the gas. It should not be absorbed by the melt, for if the melt is still absorbing sulphur, the H_2S in the gas will keep on decreasing instead of remaining constant; moreover, in most of the runs, the sulphur in the iron actually decreases. No evidence has ever been observed for the FeS going into the walls of the crucible, or for any H_2S being decomposed. The blank test for the furnace shows still further that no H_2S has been decomposed or absorbed by the molybdenum filament. A solution was finally reached from the analysis of the crucible wall.

The crucible, after using, was broken into chips. Each chip was ground on an alundum wheel so as to remove a layer of oxides from both the inside and outside surfaces. The part left, which was perfectly clean and white, was then crushed, powdered, and analyzed for sulphur in the same way as the analysis for sulphur in the melts. According to this method, the crucible from Run 25 gave 0.37 per cent sulphur, and from Run 26, 0.34 per cent sulphur. The solution left in the generating flask in which the powder was dissolved was perfectly colorless, and contained no significant amount of iron. The sulphur in the crucible must be mainly, if not entirely, a sulphide of magnesium or possibly hydrogen sulphide adsorbed by the crucible wall. The formation of magnesium sulphide, by reaction of hydro-

Table II
Results of Runs With Magnesia Crucibles

Run	Time Run Hrs.	Gas CC. Min.	Temperature Run °C.	% S Before Run	Iron After Run		$(\text{H}_2\text{S}/\text{H}_2) \times 10^3$		$\text{H}_2\text{S} \times \% \text{S} \times 10^3$	
					Condition	η , S	Entering	Leaving	Entering	Leaving
15	2	400	1558	0.667	Sound	0.740	4.2		5.67	
16	2	700	1558	0.522	Sound	6.452	1.54		3.41	
17	3	400	1558	0.6	Sound	0.350	0.709		2.02	
18	3	450	1558	0.1	Sound	0.079	0.215		2.72	
19	4.5	450	1558	1.203	Sound	1.13	5.00	3.55	4.42	3.14
20	2	750	1558	1.08	Sound	1.04	4.72	3.38	4.54	3.26
21	2	750	1558	1.04	Hollow	0.922	4.64	3.30	4.68	3.32
22	2	750	1558	0.992	Sound	0.976	4.38	3.15	4.49	3.23
25	2	750	1600	1.13	Hollow	0.900	3.60	3.11	4.00	3.46
26	2	750	1600	0.900	Pipe	0.780	3.64	2.73	4.67	3.50
23	2	750	1723	0.886	Hollow	0.704	4.16	2.89	5.91	4.11
24	2	750	1723	0.704	Hollow	0.679	4.16	2.89	6.13	4.26
32b	2.3	1000	1507	0.8	Hollow	0.816	3.11	2.75	3.81	3.37

b = Made with beryllium oxide crucible.

gen sulphide with magnesia at high temperature, is thermodynamically possible when, as in the present experiments, the gas is entirely free of water vapor.

A beryllium oxide crucible was used for Run 32. The result was the same as for magnesia crucibles, the crucible wall contained 0.36 per cent sulphur. Obviously neither magnesia nor beryllia can be depended upon for accurate results in the study of this reaction.

Runs with Porcelain Crucibles—Since basic oxide crucibles have been found to be decidedly reactive with H_2S in the gas, and cause great uncertainty for the value of the equilibrium constant, crucibles which are more acidic in nature, and, at the same time resistant to high temperature, should be used. Porcelain satisfies both of these requirements. Naturally crucibles made of porcelain or sillimanite were the next alternatives to be tried.

Table III gives the results of runs with porcelain crucibles. The equilibrium constants obtained in this case are entirely different from those obtained with magnesia crucibles, because, in addition to the lowering of H_2S in the gas, there is a reaction of the melt with the crucible (see Fig. 5). The lowering of the H_2S content in the gas is not appreciable at lower temperatures, but increases as the temperature increases; the total amount lowered is much smaller than that with magnesia crucible runs. The attack on the crucible by the melt increases with the temperature and time of run. The melt turns the crucible black and dissolves it. For example, the lower part of the crucible from Run 29, which had been heated for 6 hours, left only a very thin black crust, which barely held the melt in position. Since the porcelain is made from aluminum silicate, it is probable that the Al_2O_3 in the crucibles causes the lowering of H_2S in the gas and the reaction of the crucible with the melt.

Runs with Silica Crucibles—Since runs with magnesia crucibles gave uncertain results, and those with porcelain crucibles failed to verify them, the next type of crucibles which have decidedly no action with the H_2S in the gas, would be those made of silica. This material has a melting point of about 1700 degrees Cent. (3100 degrees Fahr.). In a chemical laboratory it is not used at a temperature higher than 1200 degrees Cent., because above this temperature the silica devitrifies and undergoes a great decrease in strength. Whether it would be serviceable for this purpose or not, could be determined only by trying it out.

Silica crucibles softened at temperatures higher than 1530 de-

Table III
Results of Runs With Porcelain Crucibles

Run	Time Run Hrs.	Gas CC. Min.	Temperature Run °C.	% S Before Run	Iron After Run Condition % S	$(H_2S/H_a) \times 10^3$ Entering Leaving	$\frac{H_2S}{H_a} \times 10^3$ Entering Leaving
27	2	750	1579	0.7	Hollow 0.746	3.50 3.09	4.69 4.14
29	6	1000	1579	0.00	Hollow 0.597	3.26 2.71	5.45 4.53
28c	2	1000	1584	1.145	Sound 0.954	3.56 3.56	3.73 3.73
43d	2	800	1584	1.25	Hollow 1.22	4.85 4.55	3.98 3.73
31	2	1000	1513	1.07	Hollow 1.002	3.15 3.15	3.14 3.14
33	2.5	750	1513	1.002	Hollow 0.935	2.95 2.95	3.19 3.19
46e	2	1000	1546	1.+	Hollow 1.290	4.88 4.46	3.78 3.46

c = Melt contained a few pieces of quartz chips.

d = With unglazed porcelain crucible.

e = With unglazed sillimanite crucible.



Fig. 5—Crucibles Before and After Run, and Typical Melts Obtained. The Photographs are Arranged to Show at the Left—Magnesia Crucibles, Center—Porcelain, and Right—Silica Crucibles, and Respective Melts.

grees Cent., and occasionally yielded, causing the iron to flow out. Although two runs have been made at 1600 degrees Cent., attempts to run at temperatures higher than this were entirely unsuccessful. At these higher temperatures, 10 to 20 minutes heating made the crucible soft and no longer strong enough to hold the molten iron in position.

Table IV gives the results of runs with silica crucibles. It is seen that the inlet and outlet gases give practically the same analysis. The crucible from each run, although devitrified badly, was clean and white (Fig. 5), showing that it had absorbed nothing from the melt.

The rate of gas used in this series of runs was from 750 to 1050

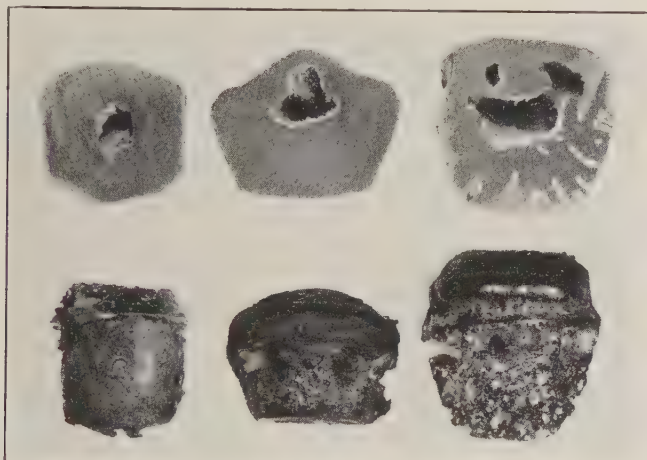


Fig. 5b—Typical Melts from Crucibles in Fig. 5.

cubic centimeters per minute. No effect on the equilibrium constant has been observed by changing the rate from 750 to 1050. An attempt has been made in Run 47 to use a gas rate of 1350 cubic centimeters per minute. At this rate the gas carried with it the sublimed amorphous silica which finally clogged the stop-cock at the outlet end, and stopped the passage of the gas entirely.

Due to the sublimation of silica, a great deal of black amorphous substance collected on the top of the crucible and on the furnace wall. This substance can be decolorized easily by immersing it in HCl , but the main bulk of the substance remained undissolved. This substance, then, must be mainly silica (possibly with some elementary silicon) colored black by iron and FeS which evaporated from the melt and finally condensed with this silica.

Since silica is slowly reduced by hydrogen at high temperatures, it is to be expected that some silicon would be absorbed by the melt. Several melts were analyzed for silica with the following results. Heat No. 52 contained 0.41 per cent; No. 49, 0.81 per cent; and No. 45, 0.86 per cent silicon. The exact effect of this silicon upon the

Table IV
Results of Runs With Silica Crucibles

Run	Time Run Hrs.	Gas CC. Min.	Temperature Run °C.	% S Before Run	Iron After Run		$(H_2S/H_2) \times 10^3$		H_2S $H_2 \times \% S$	
					Condition	% S	Entering	Leaving	Entering	Leaving
34	2.5	750	1513	0.816	Hollow	0.774	2.90	2.90	3.75	
48	2.2	1050	1535	0.00		0.227	2.11	1.35	4.88	
50	2	1050	1535	0.47	Hollow	0.520	2.10	2.08	4.00	
56	2	1050	1535	0.50	Hollow	0.609	2.50	2.45	4.03	
52	2	1050	1535	0.65	Hol. & Por.	0.618	2.10	2.20	3.56	
49	2	1050	1535	0.57	Hol. & Por.	0.541	2.11	2.20	4.07	
51*	2	1100	1535	0.67	Hollow	0.668	2.10	2.21	3.31	
39	2.3	950	1535	1.2	Sound	1.22	4.93	4.99	4.08	
53	2	1050	1546	0.46	Hol. & Por.	0.490	2.10	2.05	4.18	
47	2.1	1350	1546	1.29	Sound	0.983	4.53	4.53	4.61	
56*	2	1050	1558	0.1	Hollow	0.0733	0.42	0.37	5.05	
55	2.5	1050	1558	0.15	Hol. & Por.	0.0970	0.40	0.40	4.13	
54*	2	1050	1558	0.51	Hol. & Por.	0.568	2.11	2.12	3.73	
35	2.4	1050	1558	0.8	Sound	0.639	2.74	2.74	4.29	
58	2	550	1389	0.11	Porous	0.0925	0.40	0.41	4.44	
57	2	550	1389	1.0	Hollow	1.01	0.40	0.41	4.06	
45	2	1070	1389	1.0	Sound	1.03	4.88	4.76	4.62	
44	1.5	850	1389	1.22		a	4.85			
41	2	850	1384	1.3	Hollow	1.25	4.74	4.78	3.83	
37	1.7	750	1600	1.2	Sound	0.998	5.00	4.90	4.91	
38	2.8	800	1600	1.4	Sound	1.27	5.00	5.08	4.90	
42	0.8	930	1640	1.3		a	4.93	4.93	4.00	

*With no preheating of gas.

a = Crucible broken during run.

equilibrium determination was not ascertained, but it seems altogether unlikely that it should be appreciable. As a matter of interest, the oxygen content of two melts was determined by vacuum fusion. No. 53 contained 0.006 per cent, and No. 57, 0.009 per cent oxygen. The porosity observed in nearly all melts made in silica crucibles is unquestionably due to evolution of hydrogen on solidification.

The main source of error in this series of experiments comes

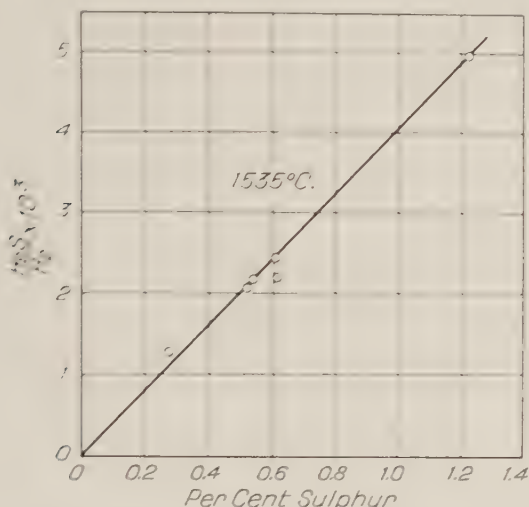


Fig. 6—Variation of Sulphur in the Iron with Ratio of H₂S to H₂ in the Gas.

from the sampling and analysis of sulphur in the melt. Most of the ingots were hollow and porous, as shown in Fig. 5. The distribution of FeS in the melt will be highly nonuniform. Unless the whole melt is analyzed, it is difficult to say that the values of sulphur analysis obtained will represent, at all times, the true composition of the melt.

DISCUSSION OF RESULTS

Form of Sulphur in Liquid Iron—The relationship between the gas and metal composition at constant temperature is shown in Fig. 6. The six points, each representing a result obtained in a silica crucible, are fitted by a straight line which shows that the percentage of sulphur is proportional to the ratio, H₂S/H₂ in the gas. This proportionality indicates clearly that the solute contains one atom of

sulphur per molecule. It is conceivable that the solute might be Fe_2S or simply atomic S, but it is far more probable that it is the compound FeS . The fact that the proportionality extends up to 1.2

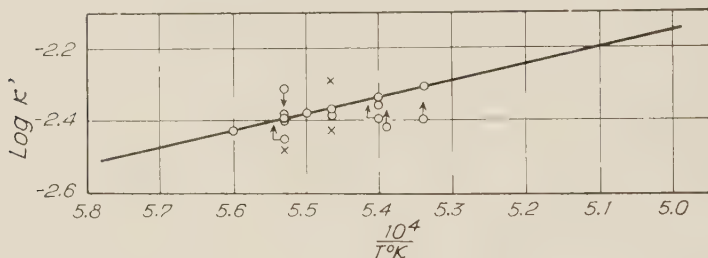


Fig. 7—Variation of Log K' with Reciprocal of Temperature. Data Obtained from Runs Using Silica Crucibles.

per cent sulphur indicates that the system conforms to the ideal solution laws up to this concentration. The results of all of these runs at 1535 degrees Cent. may be expressed by the constant,

$$K' = \frac{(\text{H}_2\text{S})}{(\text{H}_2) \times (\% \text{ S})} = 4.1 \times 10^3$$

Effect of Temperature—Results are most readily compared graphically by plotting the logarithm of K' against the reciprocal of the absolute temperature, which should, theoretically, produce a straight line. The results in silica crucibles are thus plotted in Fig. 7. Of this group, a number of runs appear definitely to have reached a state of equilibrium. This conclusion is reached from the fact that in these runs there was very little change in composition during the two hours or more of heating and the composition of the gas was unchanged by contact with the melt. These results are represented by circles. In other runs there was a distinct change in composition, indicating that the reaction was continuing and probably had not reached equilibrium during the time of the run. These points are plotted with an arrow to indicate the direction in which the reaction was progressing. The straight line drawn through the points of Fig. 7 represents our best value for the equilibrium constant in the range 1500 to 1600 degrees Cent. Its equation is:

$$\log K' = -4500/T + 0.095 \quad (2)$$

The results obtained in magnesia and porcelain crucibles are shown in Fig. 8. In these runs there was always a distinct change

in the composition of the gas as it passed through the furnace. The question arises as to whether the metal is more nearly in equilibrium with the entering or with the out-flowing gas. Both sets of points are shown in the figure, and the area between is shaded. The equilibrium line should lie within this shaded area.

It seems probable that the metal is most nearly in equilibrium

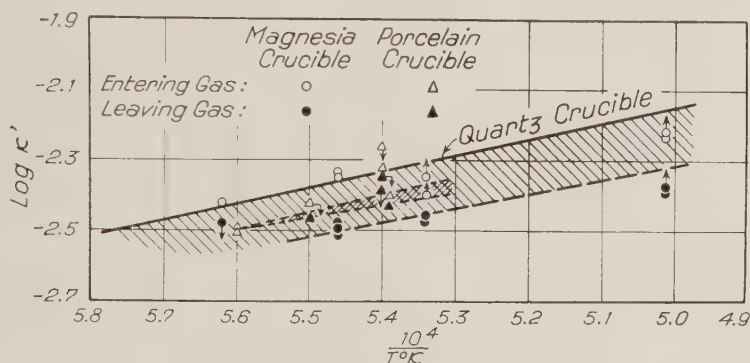


Fig. 8—Comparison of Results Obtained with Different Kinds of Crucibles.

with the entering gas, since the gas is directed toward the metal surface, and since the reaction between gas and crucible material occurs principally after the gas has passed the metal surface. The equilibrium should, therefore, be represented by the upper edge of the shaded area of Fig. 8. This edge agrees very closely with the results obtained in silica crucibles.

Comparison with Other Investigators—In order to compare the results with those of other investigators who have studied the system iron-sulphur-hydrogen, it will be convenient to express the concentrations of iron and iron sulphide in the liquid metal as mole fractions rather than as per cent. Recalculated to this basis, the results are expressed as follows:

$$K = \frac{(H_2S) \times (Fe)}{(H_2) \times (FeS)} \quad (3)$$

$$\log K = -4500/T + 1.853 \quad (4)$$

The equilibrium in the reaction of solid iron sulphide with hydrogen to produce solid iron has been studied by Jellinek and Zakowski (3), by Britzke and Kapustinsky (4), and by Bierner (5). Their results may be extrapolated to higher temperatures by the aid

of the heat capacities and heats of fusion of the substances involved in the reaction. Their data are shown in Fig. 9 by the three rather discordant lines at the left of the figure. The extrapolation of the data of Britzke and Kapustinsky (which seem to be the best of the three) to higher temperatures is indicated by the broken line. The

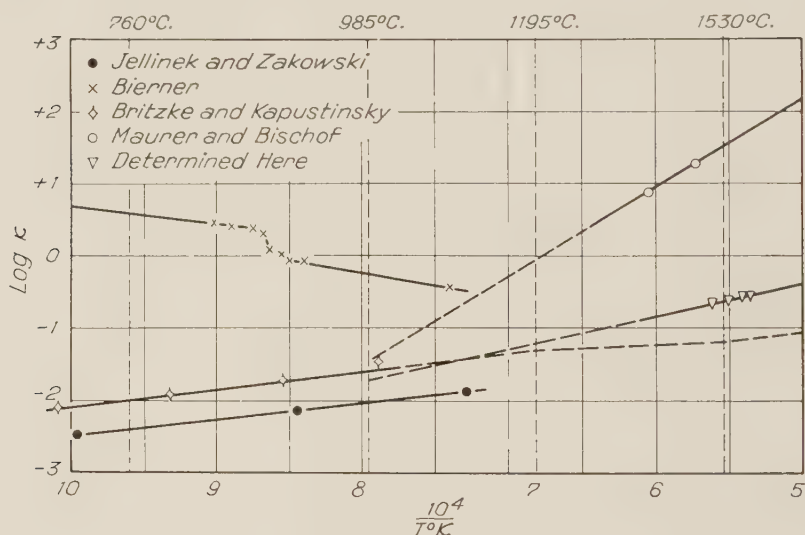


Fig. 9—Comparison of Data Obtained by Different Investigators.

extrapolation is based upon the adequate thermal data assembled by Kelley (6). Our results are shown by the triangles at the right and the heavy line drawn through them represents Equation 4. The agreement with the line extrapolated from lower temperatures is better than might have been anticipated.

The reaction in liquid iron-sulphur alloys has also been studied by Maurer and Bischoff (7), whose results are shown by the line at the upper right. Their values of K are about one hundred times as large as ours, and it would appear that the accuracy of their results has suffered from some source of error which they did not suspect. They used beryllia crucibles, and it seems probable that in their apparatus sulphur was absorbed more rapidly by the crucible than by the iron.

THERMODYNAMIC CALCULATIONS

In order to apply the results of our experiments to some of the

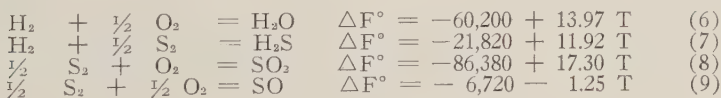
Table V
Thermodynamic Properties of Gases

	Free Energy $F^\circ - E^\circ$ $-\left(\frac{\quad}{T}\right)$		Entropy S°		Heat Capacity C_p	
	298.1	1873°	298.1	1873°	298.1	1873°
H ₂	24.436	37.21	31.23	44.49	6.89	8.07
O ₂	42.081	55.59	49.02	63.64	7.02	8.96
S ₂	47.242	61.70	54.42	70.19	7.75	8.98
H ₂ O	37.179	52.685	45.10	62.34	8.00	11.88
H ₂ S	41.174	57.31	49.15	67.67	8.12	12.67
SO ₂	50.95	69.42	59.40	81.44	9.51	13.58
SO	46.07	59.98				

practical problems of steel making, it will be desirable to assemble the available data on a number of the compounds of sulphur and the substances with which they react. The property of especial interest is the free energy, for when this is known for each substance taking part in a reaction, the equilibrium constant of the reaction is easily obtained from the change in free energy as shown by the equation,

$$\Delta F^\circ = -4.575 T \log K \quad (5)$$

Gases—The properties of the gases in which we are interested are known with considerable accuracy, thanks to recent computations based upon precise spectroscopic data. The free energy, entropy, and heat capacity of several gases at 298.1 and 1873 degrees Kelvin (25 and 1600 degrees Cent.) are shown in Table V. These data are obtained from the publications Giauque (8), Johnston (9), Gordon (10), Kassel (11), and Cross (12), and their several co-workers. The total energy, free energy, and entropy changes which accompany the formation of the gaseous compounds from their gaseous elements are shown in Table VI. From them we find the following equations which may be employed without significant error in the range 1500-2200 degrees Kelvin (2300-3500 degrees Fahr.).

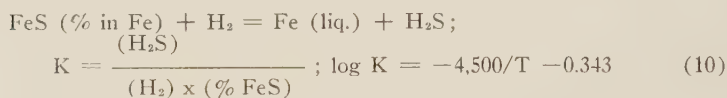


Ferrous Sulphide—The free energy of iron sulphide in liquid iron is obtained by combining the results of our experiments with Equation 7. For this purpose, the experimental results are expressed in terms of the percentage of iron sulphide in the metal and the equilibrium constants recalculated to this basis. The result is given in the

Table VI
Energy of Formation of Compounds from Their Elements

	Temp. °K.	H ₂ O	H ₂ S	SO ₂	SO
ΔE°	0.0	-57,110	-19,620	-85,860	-6,560
ΔF°	298.1	-54,637	-17,570	-81,460	-6,980
ΔF°	1873	-34,030	+ 510	-53,980	-9,060
ΔS°	298.1	- 10.64	- 9.29	- 16.83	+ ...
ΔS°	1873	- 13.97	- 11.92	- 17.30	+ 1.25
ΔH	1873	-60,200	-21,820	-86,380	-6,720

following equation, in which the symbol (% in Fe) signifies that the activity of FeS is equal to its percentage, and that its standard state is a one per cent solution in liquid iron:



The free energy change in the reaction is, therefore, (by Equation 5):

$$\Delta F^\circ = 20,590 + 1.57 T \quad (11)$$

and when this is combined with Equation 7, we find the free energy of formation of iron sulphide dissolved in liquid iron at a concentration of one per cent,

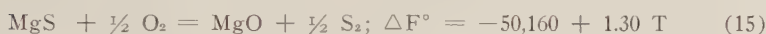


Other Sulphides and Oxides—The free energies of several sulphides and oxides will be of interest in computing the desulphurizing powers of slags. For the most part, these must be obtained from the heat of formation and entropy, and by upward extrapolation from room temperature. Although data of this sort are much less accurate than those shown above, they will serve for making some useful approximate calculations. The data in Table VII are assembled from several sources. The entropies are quoted from Kelley (13). The heats of formation of CaS and MgS are the old values of Sabatier (14), as quoted by Schenck (15), while that of MnS is a more dependable value obtained by Maier (16). The data for CaO and MgO are taken from the International Critical Tables, that of MnO is the result of a recent determination of Roth (17). The heat of formation of gaseous sulphur is that computed by Gordon (10).

Table VII
Thermodynamic Properties at 25 Degrees Cent
(ΔH in Kilo-Calories)

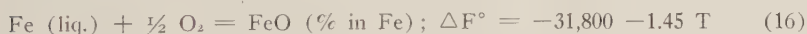
	CaO	MnO	MgO	$\frac{1}{2}$ O ₂	CaS	MnS	MgS	$\frac{1}{2}$ S ₂
ΔH	-151.8	-96.5	-145.8	0	-111.2	-45.9	-79.4	+15.54
S	9.5	14.4	6.4	24.51	13.5	18.7	...	27.21

From the data of Table VII, we obtain three useful equations which express the difference in free energy between the oxides and sulphides of the three metals.



These equations are strictly valid only at 25 degrees Cent., and the third one is uncertain with respect to the entropy of MgS. The reactions are so symmetrical that the heat effects are likely to be nearly constant, and in the absence of specific heat data, the equations may be used as approximations at the temperature of liquid steel.

The free energy of ferrous oxide in liquid iron at 1600 degrees Cent. has been accurately determined by Fontana and Chipman (2). At other temperatures it may be estimated from the approximate temperature coefficient previously reported by Chipman (18). The resultant equations for its free energy in liquid metal and slag are:



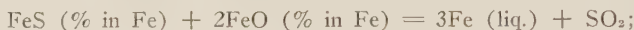
APPLICATION TO STEEL REFINING

The foregoing data are sufficient to answer many—though by no means all—of the questions which have arisen from time to time regarding the removal of sulphur from liquid steel or the prevention of its absorption.

Desulphurization with Hydrogen—The possibility of removing sulphur from liquid steel by bubbling hydrogen through the bath can be directly computed from the results of our experiments. The equilibrium constant at 1600 degrees Cent. was found to be $K' = (\text{H}_2\text{S})/(\text{H}_2 \times \% \text{S}) = 4.9 \times 10^{-3}$. If we wish to reduce the sulphur

content of iron from .040 to .020 per cent, the average H_2S content of the exit gas will be $4.9 \times 10^{-3} \times .030 = .147 \times 10^{-3}$ or about fifteen parts per hundred thousand. The removal of 0.02 per cent sulphur from one ton of steel would produce about five cubic feet of H_2S , which would require approximately 33,000 cubic feet of hydrogen. Clearly, such a process would be out of the question.

Desulphurization by Vacuum Treatment—Perhaps it might be possible to remove sulphur from an oxidized bath by melting in vacuum, and pumping off sulphur dioxide. The reaction and its free energy are obtained from Equations 8, 12, and 16:



$$\Delta F^\circ = + 19,630 + 9.85 T \quad (18)$$

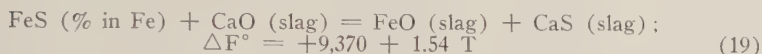
$$K = \frac{(\text{SO}_2)}{(\% \text{ FeS}) (\% \text{ FeO})^2}; \log K = -4,290/T - 2.15$$

At 1600 degrees Cent., $K = 3.6 \times 10^{-5}$, and when this is solved for a sulphur content of 0.020 and an iron oxide content of 0.36 per cent, it is found that the pressure of sulphur dioxide is 2.57×10^{-6} atmospheres or about 0.002 millimeter. A vacuum such as this is can be obtained in the laboratory, but is scarcely to be considered for melts larger than a few ounces. A similar calculation shows that the pressure of sulphur monoxide would be of the order of 10^{-8} millimeters. In fact, the data of Table VI show that in all cases at steel-making temperatures the formation of SO is altogether negligible in comparison with SO_2 .

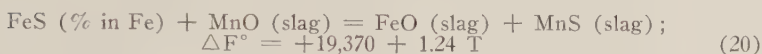
Slag-Metal Reactions—The reactions to which we owe the desulphurizing powers of basic slags are those in which a basic oxide in the slag reacts with iron sulphide in the metal to form iron oxide and a more stable sulphide. In order to write the free energy equation for such a reaction, it is necessary to combine the appropriate equation—13, 14, or 15—with Equations 12 and 17. This combination leads to the three equations and their corresponding equilibrium constants as shown below. Strictly speaking, these equations should be applied only to the solid sulphide and solid oxide of the basic element; but the energy changes involved in the fusion of the solids are small and tend to balance one another. The minor uncertainty occasioned by their omission can be corrected only when more complete data are available. For the present purposes, we shall apply the

equations to the oxides and sulphides as they exist in slags, expressing their activities as mole fractions of the free oxide or sulphide.

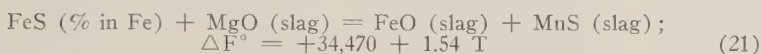
The desulphurization equations are:



$$K = \frac{(\text{FeO}) (\text{CaS})}{(\% \text{ FeS}) (\text{CaO})}; \log K = -2047/T - 0.337$$



$$K = \frac{(\text{FeO}) (\text{MnS})}{(\% \text{ FeS}) (\text{MnO})}; \log K = -4234/T - 0.271$$



$$K = \frac{(\text{FeO}) (\text{MgS})}{(\% \text{ FeS}) (\text{MgO})}; \log K = -7530/T - 0.337$$

Table VIII
Equilibrium Constants in Desulphurization by Basic Oxides

Temperature Degrees Cent.	1500	1600	1700
CaO-CaS	0.032	0.037	0.042
MnO-MnS	0.0022	0.0029	0.0038
MgO-MgS	2.6×10^{-5}	4.6×10^{-5}	7.0×10^{-5}

The equilibrium constants of the three slag-metal reactions are shown at three temperatures in Table VIII. A number of conclusions may be reached from these data. The first is that lime is a more potent desulphurizer than either of the other oxides, with MnO second and MgO a poor third. This should not be interpreted as conflicting with the data of Holbrook and Joseph (19) on blast furnace slags since the present calculations have to do with limiting conditions only, whereas their measurements involved only the speed of the reaction. A second conclusion is that an increase in temperature produces a slight increase in desulphurizing power. In general, it produces an even more marked increase in the speed of the reaction, thus exerting a double effect upon the final sulphur content of the metal.

In order to apply the calculations quantitatively to open-hearth results, it is necessary to convert percentages of lime, FeO, etc., to mole fractions in the slag. There is no recognized method of making this conversion, since the nature and degree of dissociation of the

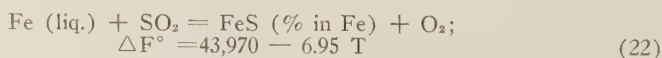
compounds in the slag are not known with certainty. As a first approximation, we may assume that in basic slag the silica is held as dibasic silicates of the type $2 \text{CaO} \cdot \text{SiO}_2$, and the phosphorus as tri-basic phosphates of the type $3 \text{CaO} \cdot \text{P}_2\text{O}_5$. The free CaO is then obtained by subtracting from the total number of moles of base, $\text{CaO} + \text{MnO} + \text{MgO}$, twice the number of moles of SiO_2 , and three times the number of moles of P_2O_5 . The data of Table IX are taken from the published work of Diehl (20). The mole fraction of CaO is computed as outlined above, while that of FeO disregards any tendency of this oxide to combine with other constituents of the slag. The total sulphur content of the slag is computed as CaS , and that of the metal as FeS . The ratio corresponding to the equilibrium constant in the lime-iron sulphide reaction is shown in the last line of the table. These figures are in agreement, at least as to order of magnitude, with the calculated equilibrium constant 0.037 at 1600 degrees Fahr. This may be taken to indicate that the desulphurization equilibrium is at least approached in open-hearth operation, and that the most important variable affecting it is the free lime.

Table IX
Desulphurizing Power of Open Hearth Slags;
Data from Diehl (20)

Heat No.	82096	93172	85241	73259	83254	83261	81292
CaO , Mol Fr.	0.317	0.197	0.129	0.420	0.507	0.537	0.547
FeO , Mol Fr.	0.192	0.183	0.236	0.252	0.207	0.230	0.250
CaS , Mol Fr.	0.0027	0.0033	0.0032	0.0081	0.0064	0.0084	0.0112
FeS Metal % (FeO) (CaS)	0.102	0.099	0.069	0.126	0.091	0.093	0.113
(% FeS) (CaO)	0.016	0.031	0.085	0.038	0.029	0.039	0.045

Reactions Between Gas and Bath—A number of reactions may occur by which sulphur is transferred from combustion gases to the slag and to the metal. In the flame practically all of the sulphur in the fuel is converted into sulphur dioxide, and it will be unnecessary to consider either H_2S , S_2 , or SO . This statement may easily be verified by simple computations based upon Equations 7, 8, and 9.

The reaction by which Herty (21) and Maurer and Bischoff (7) account for absorption of sulphur from the gases is written below, along with its free energy expression obtained by combining Equations 8 and 12:

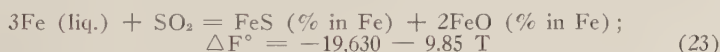


When this is solved for a temperature of 1800 degrees Kelvin (2780 degrees Fahr.), the melting point of iron, we find

$$K = \frac{(\text{O}_2) (\% \text{ FeS})}{(\text{SO}_2)} = 1.5 \times 10^{-4}$$

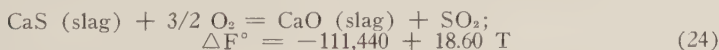
If this is the controlling reaction, then in a gas mixture containing as much oxygen as sulphur dioxide no sulphur pick-up should occur above 0.00015 per cent FeS, and any sulphur in excess of this amount should be oxidized to SO₂. Why, then, does sulphur absorption occur? If the above reaction is effective, why can't we desulphurize the bath by providing a little excess air in the flame? The answer is that the reaction is not effective because the oxygen which comes in contact with the iron is all used up in forming iron oxides. An oxidizing flame is conducive to desulphurization or to a decreased sulphur pick-up, but the mechanism is more indirect than Equation 22 would indicate.

The reaction of iron with sulphur dioxide is more correctly represented by the equation,



The equilibrium constant at the melting point is 2.3×10^4 , which signifies that sulphur dioxide in contact with the iron would be almost entirely absorbed. A function of excess air is, therefore, to prevent this contact during melting by producing a protective oxide film.

When the bath is covered by slag so that the gases do not come into intimate contact with the metal, some removal of sulphur from the slag by oxidation may occur. The reaction is,



The equilibrium constant at 1600 degrees Cent. is about 2×10^9 and the reaction, therefore, has a strong tendency to occur. Other substances in the slag are competing with CaS for the small amount of oxygen that is available. Suspended droplets of iron are being oxidized, FeO absorbs oxygen to form Fe₂O₃, and finally the CO evolved from the bath is burning to CO₂. It is the interference of these reactions which prevents efficient desulphurization of the slag by excess air in the flame.

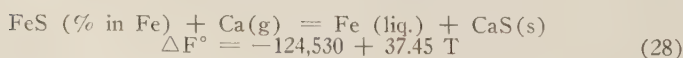
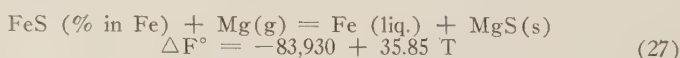
Metallic Desulphurizers—The affinity of some metals for sul-

phur is so great that under proper conditions it should be possible to effect a marked reduction in sulphur content by addition of the metal itself. It is well known that manganese will decrease the sulphur content of high-sulphur pig iron by forming manganese sulphide, which is thrown out of solution with the kish. In the open hearth, however, the desulphurizing power of manganese is offset by the reaction of its sulphide with FeO to form manganese oxide. If we compute, thermodynamically, its desulphurizing power, we find the same result as if we had based the calculation on a concentration of MnO in the slag which is in equilibrium with manganese in the metal. In the open-hearth, we cannot, in the present state of our knowledge, differentiate between the desulphurizing power of manganese and that of its oxide. Since the usual slag contains much more CaO than MnO, and since the desulphurizing power of the former is distinctly greater, we must conclude that the influence of manganese as a desulphurizer in the open hearth is far less important than that of lime. This conclusion is in agreement with the experimental results and critical discussion of Bardenheuer and Geller (22).

Calcium and magnesium form stable sulphides, and, in a bath which has been thoroughly deoxidized, their desulphurizing powers might be used to advantage. It is possible to compute the concentration of FeS which would be left in the bath, if enough calcium or magnesium is added to react with substantially all of the oxygen and to leave the bath saturated with the free metal after equilibrium with sulphur has been established. Calcium and magnesium are gases at the temperature of liquid steel, and their solubility in the bath is quite limited. The free energy of formation of the oxides from the respective gaseous metals and oxygen was used in computing their deoxidation equilibria (18). The equations are,



When these equations are combined, respectively, with 15 and 13, and the result added to Equation 12, the following expressions are obtained:



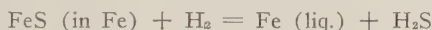
The equilibrium constants obtained from these equations for a temperature of 1600 degrees Cent. are:

$$\begin{array}{ll} (\% \text{ FeS}) & (\text{Mg}) = 1.1 \times 10^{-2} \\ (\% \text{ FeS}) & (\text{Ca}) = 4.3 \times 10^{-6} \end{array}$$

If the bath is saturated with the metal so that the partial pressure of the gaseous metal is one atmosphere, then (Mg) and (Ca) are equal to unity, and the percentage of FeS in the bath is equal to the value of the product. Thus, the sulphur present as FeS is reduced to 0.0045 per cent by the magnesium reaction or to an astonishingly low value of 1.8×10^{-6} per cent by desulphurization with calcium.

SUMMARY

A thorough study has been made of the condition of equilibrium in the reaction,



The precautions necessary for obtaining dependable equilibrium data in this reaction are described in detail, and the results of numerous experiments are presented, in which equilibrium is approached from the high-sulphur and low-sulphur sides.

The experimental data are summarized by the equation,

$$K' = (\text{H}_2\text{S})/(\text{H}_2) (\% \text{ S}); \log K' = -4,500/T + 0.095$$

The results are somewhat higher than would be expected from extrapolations of low-temperature data, but are about a hundredfold lower than the data of Maurer and Bischoff on the same reaction.

The free energies of FeS and a number of other sulphides and oxides are computed from the experimental results and from data in the literature.

The thermodynamic treatment of several possible reactions involving sulphur in liquid iron shows that:

1. Removal of sulphur from liquid steel by hydrogen requires so much hydrogen as to make the process impracticable.
2. Removal of sulphur by vacuum treatment would require a high vacuum obtainable only in very small furnaces.
3. In the desulphurization of liquid steel by slag in the open-hearth process, the most important variable is the free

lime in the slag. MnO and MgO are less potent desulphurizers. An increase in temperature promotes desulphurization.

4. In the open-hearth flame, sulphur exists as sulphur dioxide. This gas is completely absorbed when it comes in contact with liquid iron. Excess oxygen in the gas helps to prevent its absorption by formation of an oxide film. Oxygen tends to desulphurize the slag by oxidizing calcium sulphide to sulphur dioxide.

5. The desulphurizing power of metallic manganese is essentially equivalent to that of an equilibrium amount of manganese oxide in the slag. Magnesium and calcium exert a powerful desulphurizing action, provided oxygen is absent.

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